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PREPARATIVE METHODS FOR ALLOYS USING SULFUR

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PREPARATIVE METHODS FOR ALLOYS USING SULFUR

(Presented by Academician A. M. Kuliyev)

ABSTRACT

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An alternative to the conventional methods for preparing alloys and solid is offered for highly volatile components. As usual, the materials are placed in an evacuated ampule, but the furnace is at first inclined in a semihorizontal position, creating a temperature gradient that is controllable by raising or lowering the ampule in the furnace. Subsequently, the entire arrangement is righted, and the process continues according to the conventional vertical method, except that at first a difference in temperature is maintained, eventually going over to a uniform temperature. The outcome is the synthesis of more alloy in a given time with safety. The authors were able to prepare 18 to 20 g of gallium sulfides (GaS and Ga_2S_3) in two to four hours using the method described.

A variety of methods are available for the synthesis of binary and more /13
complex semiconducting alloys and compounds (refs. 1 to 4). These methods of synthesis are briefly examined and evaluated in references 5 and 6.

At the present time, the majority of synthesizing procedures are conducted by the direct method in vacuum, including primarily the following: a) one-temperature synthesis; b) two-temperature horizontal synthesis; c) two-temperature vertical synthesis.

*Numbers in the margin indicate pagination in the original foreign text.

Moreover, vibration can be applied, which tends to speed up the time for synthesis 10- to 20-fold and permits the preparation of more compact ingots with a coarse-grained crystalline structure (ref. 5).

If in synthesis one of the components is highly volatile, two-temperature synthesis is recommended.

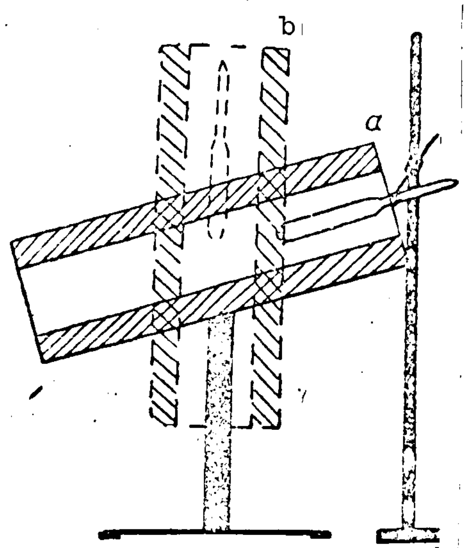
By applying the above-indicated methods, however, we were not able to synthesize more than one gram of the sulfides safely and quickly.

The following are some typical shortcomings of the methods. In the horizontal two-temperature synthesizing method with vibration, elemental sulfur remains in the colder region of the vessel, not taking part in the reaction. This makes it difficult to obtain completely stoichiometric alloys, consumes a great deal of time, the resultant ingots do not have a definite shape, and, finally, the alloy smears the walls of the vessel.

In vertical synthesis, despite steady vibration treatment, the surface of the molten gallium is coated with sulfides, which have a high melting point. This means that there is not sufficient gallium to combine with the sulfur, hence an excess of sulfur remains. In addition, the small area of contact between the sulfur and the metal slows down the reaction rate considerably. As indicated by Gadzhiyev, Nadzhafov, and Sharifov (ref. 6), the application of vibration and two-temperature synthesis does not permit the safe synthesis of the gallium sulfides with more highly volatile components. These authors, elaborating the method of Fischer (ref. 7) for synthesis with highly volatile com- /14
ponents, suggest a calorimeter, which does not seem to have too much utility. On the one hand, the resultant alloys and compounds are noncompact and smear the walls of the vessel, on the other hand, the method is very difficult to put into practice experimentally.

For the case of synthesis of GaS and Ga_2S_3, the so-called visual combining method has been developed, which is essentially contained in the following.

An evacuated quartz ampule 20 to 22 cm long is filled with a calculated quantity of the initial materials (metallic gallium and elemental sulfur). The ampule is then placed in a Nichrome wire mesh. In the first stage of synthesis, the ampule is placed in a semihorizontal furnace so that the empty part of the tube is higher (figure, position a) and remains outside (projecting about 3 to 5 cm). The temperature in the furnace is gradually raised above the melting point of the substance to be synthesized, creating a temperature gradient between the parts of the ampule inside and outside the furnace. As the temperature in the furnace is increased, the temperature in the outside part of the ampule is regulated by raising or lowering it in the furnace.



At higher temperatures air cooling is not sufficient to maintain a definite temperature gradient, so cooling is realized by asbestos moisteners.

The degree of immersion of the ampule in the furnace is regulated visually by hand, judging from the quantity of sulfur in the molten state that is returned to the reaction zone due to the sloping position of the ampule. Inside the oven, at high temperatures, a reaction takes place between the liquid gallium and the sulfur vapor. The contents of the ampule are agitated periodically by hand.

As the reaction progresses, the ampule is gradually lowered into the furnace, so that at the end of the reaction the entire ampule is now inside it. Then begins the second part of the synthesis, namely a changeover to vertical one-temperature synthesis (figure, position b). For this, the furnace is moved up to the vertically upright position, without removing the mesh. In the first few minutes, a portion of the ampule remains outside until the last traces of sulfur have disappeared, and as the latter diminish the ampule is submerged into the furnace.

This method can be used to synthesize more than 18 g of gallium sulfides in one batch in two to four hours. We synthesized GaS and Ga_2S_3 in this fashion. No free sulfur was left after synthesis (as verified by chemical analysis). Thermograms and powder diagrams of the prepared substances are entirely consonant with the data given in the literature.

The melting points of the synthesized GaS and Ga_2S_3 were found to be equal to 965 and 1120 ± 10°C, respectively.

CONCLUSION /15

1. The method of horizontal two-temperature synthesis has been replaced by a semihorizontal two-temperature method, whereby a temperature gradient is produced by the use of a single furnace.

2. The temperature of the outside, projecting part of the ampule is regulated visually, judging from the quantity of condensed sulfur (or other highly volatile component).

3. From the semihorizontal two-temperature mode, direct transition is made, first to the two-temperature, then to the one-temperature vertical mode. The same single furnace as was used in the first stage of the operation is used here.

4. Clearly, this method of synthesis could be used for other systems as well, where one of the components is a highly volatile material. We are of the opinion that the application of vibration would shorten the time for synthesis.

5. The simplicity of the synthesizing apparatus is an attractive feature of the method.

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